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US 4067791A
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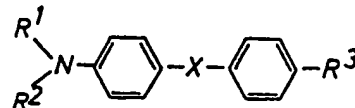
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(54) Photopolymerisable materials
and recording method

(57) A photosensitive material is
described which comprises a base and
a photosensitive layer comprising a
photopolymerisable compound and as
photopolymerisation initiators an
oxime ester and a p-
dialkylaminobenzene of the formula



wherein R¹ and R² are lower alkyl, R³ is
hydrogen, alkyl, alkoxy or N(R¹)(R²)
and X is —CO—, —CS—, CH₂, or
—CH(OH)—. Improved sensitivity is
obtained by the presence of the p-
dialkyl aminobenzene compound.

3??

1, 2, 4-5, 6, 9, 12-13, 14, 15, 16, 18

Certain of the chemical
formulae appearing in the
printed specification were
submitted in formal form after
the date of filing.

GB 2 029 423A

SPECIFICATION

Improved photopolymerisable materials and recording method.

The present invention relates to improved photosensitive materials and to methods for recording relying on the use of layers of photopolymerisable compositions.

Photopolymerisable compositions are known which comprise addition polymerisable ethylenically unsaturated compounds and an addition polymerization initiator activatable by actinic radiation. A variety of applications have been described for these photopolymerisable compositions. The photopolymerisable compositions can be applied e.g. as photosensitive layer on surfaces of metal or of other materials. Upon exposure to actinic radiation through a suitable image pattern, the radiation induces polymerisation in the exposed areas of the photopolymerisable layer, whereby the exposed areas are rendered insoluble in the solvent or solvents used for applying the photopolymerisable layer. Thereafter the non-exposed areas are washed away with a solvent for the ethylenically unsaturated monomeric material. In this way can be formed planographic printing plates, matrices for printing matter, screens for silk-screen printing, and photo-resists for etching.

Many photopolymerisation initiators which under the influence of actinic light increase the photopolymerisation rate have already been described. For example in US-P 3,558,309 photopolymerisable compositions have been described that comprise as initiator oxime esters. In USP 3,847,610 compounds comprising at least one diazosulphone group are used as initiator. Compounds containing at least one diacyldiazomethane group are the initiators used according to US-P 3,682,642.

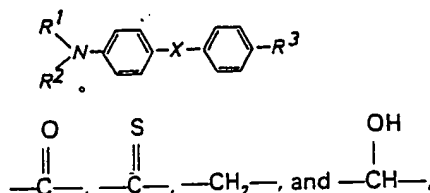
New photoinitiators are constantly being sought for to fulfil particular requirements such as stability or compatibility in a particular composition and/or to increase the speed of photopolymerisation. Particularly in the field of image recording e.g. in the graphic arts field it is highly desirable to dispose of recording material that have a high photosensitivity and that are easily and rapidly processable e.g. by automatic wash-off processing by means of a solvent and preferably by means of a mere aqueous alkaline liquid.

It has been attempted to increase the photopolymerisation rate by the use of a combination of photoinitiators. From US-P 3,549,367 it is known that the combined use of p-aminophenylketones e.g. Michler's ketone with lophinedimers in particular 2,4,5-triarylimidazolyldimers in the photopolymerisation of ethylenically unsaturated compounds, gives a synergistic response, the resultant performance being greater than a simple additive function.

On the contrary, the p-aminophenylketones have no influence on the photopolymerisation rate of photosensitive materials based on the use of photopolymerisable ethylenically unsaturated compounds and as initiator a compound containing at least one diacyldiazomethane group as described in US-P 3,682,642, or a compound containing at least one diazosulphone group as described in USP 3,847,610. Moreover, Michler's ketone acts as a photopolymerisation inhibitor on the photopolymerisation in bulk liquid photopolymerisable compound containing dispersed or dissolved therein an oxime ester, as well as on the photopolymerisation in aqueous or organic solution of an ethylenically unsaturated compound and the said oxime ester.

It was therefore very surprising to find that p-aminobenzene compounds as defined hereinafter including p-aminophenylketones, substantially enhance the photoinsolubilisation rate of a photosensitive recording layer comprising a photopolymerisable ethylenically unsaturated compound and an oxime ester as photopolymerisation initiator. Thus, the combination of the oxime ester and the p-aminobenzene compound in a photosensitive recording layer comprising a photopolymerisable compound gives a synergistic response upon image-wise exposure of the layer.

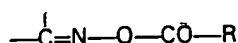
According to the invention a photosensitive material is provided which comprises a base having thereon a photosensitive layer comprising a photopolymerisable, ethylenically unsaturated organic compound or compounds and an oxime ester photopolymerisation initiator characterised in that the layer contains as additional initiator a p-dialkylamino benzene corresponding to the formula:



wherein X represents

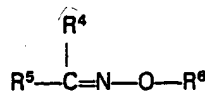
each of R^1 and R^2 , the same or different, represents a lower ($\text{C}_1 - \text{C}_9$) alkyl group, and R^3 represents hydrogen, an alkyl group, an alkoxy group or a $\text{N}(\text{R}^1)(\text{R}^2)$ group wherein each of R^1 and R^2 has one of the above meanings.

By the term "oxime ester photopolymerisation initiator" is meant a compound containing at least one oxime ester group of the following structure:



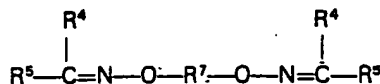
wherein R is an organic group. An alternative term for "oxime ester" is "O-acyloxime".

Specific oxime esters which can be used as photopolymerisation initiator can be represented by the following formulae:



$\text{R}^6 = \text{H}$

5 and



5

wherein:

R⁴ represents an alkyl group comprising 1 or 2 carbon atoms, an aryl group, an alkaryl group, an aralkyl group, a hydroxy-substituted aralkyl group, or a substituted or unsubstituted acyl group,

10 R⁵ represents a hydrogen atom, an alkyl group comprising 1 or 2 carbon atoms, an aryl group, or a substituted or unsubstituted acyl group

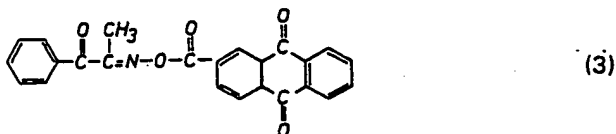
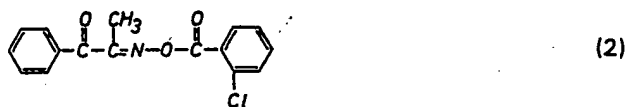
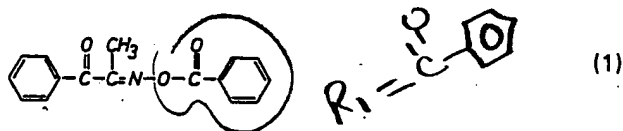
or wherein R⁴ and R⁵ together represent the necessary atoms to form with the adjacent carbon atom a cycloalkyl group, a phenanthrone group, or an indanone group,

R⁶ represents a substituted or unsubstituted acyl group, and

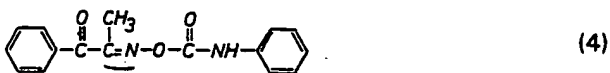
15 R⁷ represents a diacyl group.

Preferably at least one of R⁴ and R⁵ is an acyl group. The acyl groups for R⁴, R⁵ and R⁶ are preferably acyl groups derived from aliphatic or aromatic carboxylic or sulphonic acids e.g. benzoyl, phenylsulphonyl, naphthoyl, 2-anthraquinonyl-carbonyl, acetyl, propionyl, phenylacetyl, cinnamoyl, alkoxy-carbonyl e.g. ethoxycarbonyl and N-substituted carbamoyl e.g. N-phenylcarbamoyl.

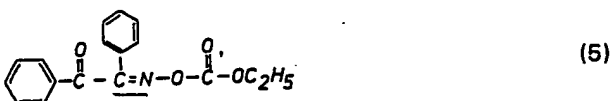
20 Suitable compounds containing at least one oxime ester group, the so-called oxime esters or O-acyloximes, are those disclosed in the above USP 3,558,309. Particularly useful are the following:



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Suitable dialkylamino benzenes corresponding to the above formula are:

4-dimethylamino benzophenone

4,4'-bis(dimethylamino)-benzophenone (Michler's ketone),

30 4,4'-bis(dimethylamino)-benzhydrol,

4,4'-bis(dimethylamino)-diphenylmethane,

4,4'-bis(dimethylamino)-benzothiofenone.

30

The photosensitive layer may comprise one or more ethylenically unsaturated polymerisable compounds such as styrene, acrylamide, methacrylamide, methyl methacrylate, diethylaminoethyl methacrylate, and acrylonitrile. When two of these monomers are used in the same photopolymerisable layer, copolymers are formed during the photopolymerisation. It is further presumed that in the case

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where the photopolymerisable material is used together with a polymeric binding agent, graft copolymers are formed between the polymeric binder and the photopolymerised material.

The photopolymerisable composition may also comprise one or more unsaturated compounds having more than one carbon-to-carbon double bond, e.g. two terminal vinyl groups, or of a polymeric compound having ethylenic unsaturation. During polymerisation of these compositions usually cross-linking will occur by means of the plurally unsaturated compound. Examples of polymeric compounds containing ethylenically unsaturation are, e.g., allyl esters of polyacrylic acid, maleic esters of polyvinyl alcohol, polyhydrocarbons still containing carbon-to-carbon double bonds, unsaturated polyesters, cellulose acetomaleates, and allylcellulose.

The photosensitive layer of the present invention preferably comprises plurally unsaturated polymerisable compounds examples of which are:
divinylbenzene,
diglycol diacrylates,
N,N'-alkylene bis-acrylamides
triethyleneglycol-diacrylate,
triethyleneglycol dimethacrylate,
pentaerythritol triacrylate
pentaerythritol tetraacrylate,
trimethylolpropane trimethacrylate,
bisphenol A-diacrylate.

The ratio of oxime ester to dialkylamine benzene can vary between wide limits and the most suitable ratio can easily be determined by running a series of tests. Generally the ratio is comprised between 1:1 and 10:1. The mixture of photopolymerisation initiators is generally used in an amount between 10 and 50% by weight with respect to the amount of photopolymerisable monomer(s).

A base of support may be coated with a solution of the ethylenically unsaturated organic compound in a solvent therefor, this solution containing in dissolved state or homogeneously dispersed therein a photopolymerisation initiating mixture of an oxime ester and of a dialkylamino benzene as defined hereinbefore, whereupon the solvent or solvent mixture is eliminated by known means such as evaporation, leaving a more or less thin coating of the ethylenically unsaturated organic compound on the base or support. The thickness of the dried photosensitive recording layer is preferably in the range of 0.5 to 5 μm . Thereafter the dried photopolymerisable coating can be exposed to actinic light rays.

The photosensitive recording layer may be exposed to any source of radiation providing UV-radiation, more particularly radiation of wave-lengths in the range of 250-400 nm, preferably in the wave-length region of 300-400 nm. Suitable light sources include carbon arcs, mercury vapour lamps, fluorescent lamps, argon glow lamps, photographic flood lamps and tungsten lamps. Moreover, ordinary daylight may also be used. Pulsed xenon lamps and tungsten lamps mainly emitting in the visible light range and to a minor amount in the ultraviolet region may likewise be used.

It is desirable that the photopolymerisable composition comprises a carrier or binding agent for the ethylenically unsaturated organic compound, and the photopolymerisation initiating mixture of oxime ester and of dialkylamino benzene. By the presence of this binding agent the properties of the light-sensitive layer are of course influenced. The choice of the binding agent is dependent on its solubility in solvents which can also be used as solvents for the ethylenically unsaturated compounds, for the oxime ester and the dialkylamino benzene.

Suitable binding agents are, e.g. polystyrene, polymethyl methacrylate, polyvinyl acetate, polyvinylbutyral, partially saponified cellulose acetate and other polymers that are soluble in solvents for the initiators and monomers. Water-soluble polymers can also be used such as gelatin, casein, starch, carboxymethylcellulose, and polyvinyl alcohol. The ratio of photopolymerisable monomer to binding agent obviously also influences the photopolymerisation. The larger this ratio the higher the photopolymerisation rate generally will be for one and the same ethylenically unsaturated organic compound.

In a preferred embodiment of the invention the photosensitive layer comprises as binding agent an alkali-soluble polymer. In that case the photosensitive recording layer, after exposure to light may be developed in aqueous alkaline medium so that the use of expensive and sometimes inflammable organic solvents for washing away the unexposed areas of the photosensitive layer is avoided.

As alkali-soluble polymers can be used copolymers with units of unsaturated monocarboxylic acids, e.g. acrylic acid, methacrylic acid, and crotonic acid, unsaturated dicarboxylic acids e.g. maleic acid, fumaric acid, itaconic acid, and citraconic acid as well as half-esters and half-amides of these dicarboxylic acids. These unsaturated carboxylic acids are copolymerised with ethylenically unsaturated compounds, which are substantially insoluble in alkaline medium and which are present in the copolymer in such a proportion that the copolymer itself remains soluble in alkaline medium. Ethylenically unsaturated compounds that can be used for the copolymerisation are styrene and derivatives thereof, vinyl chloride, vinylidene chloride, vinyl esters such as vinyl acetate, acrylates, methacrylates, acrylonitrile, methacrylonitrile e.g. copoly(ethylene/maleic acid) and copoly (methyl methacrylate/methacrylic acid).

Especially suitable are the alkali-soluble copolymers of methyl methacrylate and methacrylic acid

wherein the ratio by weight between the monomeric units varies between about 90:10 and about 75:25, more preferably between 85:15 and 80:20, and wherein the intrinsic viscosity of the copolymers measured in tetrahydrofuran at 20°C is comprised between about 0.05 and about 0.20 dl/g, corresponding to molecular weights of about 700 to 40.000.

5 These alkali-soluble copolymers of methylmethacrylate and methacrylic acid offer at the same time easy removability of the non-exposed portions and good mechanical strength i.e. resistance to abrasion of the exposed portions. 5

The photosensitive layer according to the present invention comprises according to the preferred embodiment a photopolymerisable ethylenically unsaturated (preferably plurally unsaturated) organic compound, examples of which have been given hereinbefore, a mixture of an oxime ester 10 photopolymerisation initiator and a p-dialkylamino benzene photopolymerisation initiator as defined hereinbefore, and an alkali-soluble copolymer of methylmethacrylate and methacrylic acid as defined hereinbefore. The layer preferably has a thickness comprised between 0.5 and 5 µm. 10

The proportions in the photosensitive layer of alkali-soluble polymer and of (preferably plurally) unsaturated polymerisable compound are preferably such that an ultra-violet exposure of said layer of 15 maximum 1 minute can effect at room temperature (20°C) a decrease of the exposed parts such that these parts do not dissolve in an aqueous solution (20°C) of 0.5 to 3% by weight of sodium hydroxide within 20 seconds. Weight ratios of alkali-soluble polymer to (preferably plurally) unsaturated polymerisable compound between 1:2 and 5:1 are preferred. 15

20 The amounts of oxime ester and of dialkylamino benzene added to the mixture of alkali-soluble polymer and of (preferably plurally) unsaturated compound may also vary between wide limits. Good results are obtained with 0.5—5% by weight of dialkylamino benzene and 2.5—10% by weight of oxime ester, preferably 1.5—2.5% by weight of dialkylamino benzene and 5—7.5% by weight of oxime ester, reckoned on the joint weight of alkali-soluble polymer and of (plurally) unsaturated compound. 20

25 The base of the photosensitive recording material of this invention may be coated with a photosensitive layer at one or both sides and may be made of any material as long as it does not deleteriously affect the photopolymerisation process. Typical flexible sheet materials are paper supports, e.g., coated at one or both sides with an alpha-olefin polymer, e.g. polyethylene. It is also possible to use cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene 30 terephthalate) film, polycarbonate film, poly-alpha-olefins such as polyethylene and polypropylene film, and related films such as a drawing film e.g. of the type described e.g. in the US-P 3,115,420 and 3,627,563. The support is usually about 0.05 to 0.15 mm in thickness. 30

If the base is made of a transparent resin or glass, transparencies can be made starting from photosensitive layers containing dyes or pigments. These transparencies may be used for projection, 35 e.g. with an overhead projector. If the support is an opaque paper, e.g. baryta coated paper, and the photosensitive layers contain dyes or pigments, opaque colour proofs can be made by washing-off. If the support is made of metal a photoresist can be prepared with a photosensitive coating according to the present invention, which resist may be used as etch-resist. 35

Metal bases or bases coated with metals such as e.g. zinc, and especially aluminium, are 40 excellently suited as base materials for a planographic printing plate. For the production of a planographic printing plate there may be likewise used plates of stone or glass and specially treated sheets of paper or polymeric film supports coated with a metallic layer that in its turn is coated with the photosensitive recording layer. For use in the production of intaglio or relief printing plates, metal base materials suited for etching are used, e.g. metal plates or drums of zinc, copper, steel or an etchable magnesium alloy. 45 For use in the production of printed circuits the photosensitive composition is applied, e.g., to a supported copper layer, which can be easily etched. 45

In the production of miniaturized integrated electrical components the photosensitive composition serves to form a shielding pattern, e.g., on a semiconductor substrate or insulator wherein by techniques such as vapour deposition, oxidation, ion implantation, electrodeless deposition, ion-milling or etching, 50 matter is added or removed to offer the desired electronic properties to the non-shielded material. 50

As is apparent from the above the photosensitive coating can be used in a large variety of applications.

Photosensitive materials according to the present invention are particularly suitable for the production of micro-images. For that purpose the photosensitive coatings are applied to a relatively thin 55 highly opaque black or grey metal coating on a film support, the metal coating being etchable and thus serving as imaging layer. Suited metal coatings are tellurium and tellurium alloy coatings having a thickness preferably in the range of 50 nm to 500 nm and bismuth coatings having a thickness preferably in the range of 25 nm to 300 nm. 55

According to one embodiment in the composition of the metallic imaging layer tellurium alloys 60 comprising at least 50 atomic percent of tellurium are used. Typical tellurium compositions, which are etchable with an aqueous hypochlorite solution are e.g. described in the published German Patent Application (DE-OS) 2,723,613. 60

According to another and more preferred embodiment the imaging metal layer consists of bismuth. Bismuth possesses the advantage of directly adhering to organic resin supports such as a 65 polyethylene terephthalate support when deposited thereon from bismuth vapour under reduced 65

pressure conditions. Typical bismuth coatings have been described in DE-OS 2,723,613.

Vapour deposition techniques are sufficiently known to those skilled in the art e.g. of preparing photoconductive selenium coatings (see e.g. US-P 3,874,917 of Charles Wood, John C Schottmiller and Francis W. Ryan and US-P 3,884,688 of John C. Schottmiller and Francis W. Ryan).

5 Bismuth forms a black, non-light-reflecting coating showing no crazing and it provides a very high spectral density. Indeed, a bismuth layer already at a coating thickness of 80 nm shows a spectral density of about 3. A 100 nm bismuth layer has a spectral density of about 5.

10 A bismuth layer for a recording material according to the present invention is preferably applied to a polymeric film support, e.g. a sheet or belt. Preferably a polyethylene terephthalate support, e.g. of 0.07 to 0.1 mm thickness, is used.

15 The photosensitive materials according to the present invention are prepared by coating the ingredients forming a photosensitive layer to the selected substrate by a known coating technique, e.g. by spin-coating, whirl-coating, spraying, dip-coating, roller-coating, air-knife coating, doctor-blade coating, etc. The coating composition may comprise besides the ingredients referred to hereinbefore matting agents e.g. silica particles in association with urea-formaldehyde resin e.g. of the type described in US Patent Application 4479/78, polymethylmethacrylate particles, etc., antistatic agents, coating aids e.g. anionic, cationic and surface active agents, silicon oils, etc.

Before their application in the form of a coating these ingredients are dissolved preferably in a low-boiling solvent, e.g. acetone, that after the coating step is removed by evaporation.

20 The thickness of the dried photosensitive layer may be in the range of 0.5 to 20 μm but is preferably between 1 and 5 μm .

25 The present invention includes a recording method comprising the steps of information-wise exposing to actinic radiation a photosensitive material comprising a base coated with a photosensitive layer as referred to hereinbefore whereby in the exposed areas at least one ethylenically unsaturated compound(s) is or are polymerised (copolymerised) and removing the non-exposed or insufficiently exposed portions of the layer by washing with a solvent for the ethylenically unsaturated compound(s).

The present invention includes a recording method in which the photosensitive layer is used to form metal images. Said method includes the steps of:

- 30 (1) information-wise exposing to actinic radiation in particular UV-radiation a recording material comprising a transparent film support bearing an opaque metal coating and thereover an alkali-soluble photosensitive layer as hereinbefore defined,
- (2) overall contacting the photosensitive layer with an aqueous alkaline liquid to remove selectively the non-exposed or insufficiently exposed portions of the photosensitive layer, and
- 35 (3) contacting the bared portions of the opaque metal layer with a liquid that is capable of chemically removing said portions without removing the exposed portions of the photosensitive layer.

The exposure may be an exposure through a contacting transparent master pattern or a projection exposure.

40 The concentration of alkaline substance, e.g. potassium hydroxide, used for developing the resist layer, i.e. for selectively removing the unexposed photosensitive layer portions, may vary widely. Thus, e.g. 0.4 to 7.5% by weight aqueous solutions of potassium hydroxide may be used.

Other alkaline substances which may be used for washing away the non-exposed portions of the photosensitive layer include 0.25 to 5% aqueous solutions of sodium hydroxide and 1 to 10% aqueous solutions of potassium carbonate.

45 For the chemical etching of a tellurium-containing layer preferably aqueous solutions of 0.5 to 30% of sodium hypochlorite are used.

For the etching of a bismuth layer preference is given to aqueous acidic iron (III) chloride solution. The concentration of iron (III) chloride is, e.g., in the range of 5 to 20% by weight. Said solution contains preferably from 0.25 to 1% by weight of citric acid.

50 A likewise useful etching solution for the removal of bismuth is an aqueous solution containing 3 to 6% by weight of hydrogen peroxide and 5 to 10% by weight of sulphuric acid. Instead of hydrogen peroxide sodium perborate or urea peroxide, e.g. $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ and $\text{NH}_2\text{CONH}_2 \cdot \text{H}_2\text{O}_2$ can be used.

55 The processing of the photo-exposed recording materials of the present invention is advantageously carried out in an automatic processing apparatus, in which the material is transported automatically through processing stations in which the removal of the still soluble portions of the photosensitive layer and the etching (if necessary) of the bared imaging layer portions take place in successive stations.

60 For example in a particularly suitable processing apparatus for use in the production of metal-images e.g. bismuth-images according to the present invention, a first station comprises a tray for holding an appropriate alkaline aqueous liquid, through which the exposed recording material is transported. After the alkaline development stage the surplus alkaline liquid absorbed in and adhering to the material is removed by passing the developed material through a second tray filled with plain water, whereupon the material is led through a third tray containing a suitable etch solution for the bared portions of the metallic imaging layer. Processing is completed by carrying the material through a fourth tray containing plain water for rinsing the material. Processing preferably proceeds at room

temperature (about 18 to about 25°C) but may proceed at higher temperatures. Care must be taken, however, not to damage the photosensitive layer.

The alkaline developing station and etching station can be arranged separately but preferably they are grouped in a compact unit, in which the recording material is carried automatically at a constant speed from the alkaline developing tray into the other trays.

The total processing for the formation of the metal images in said trays normally lasts but about 30 seconds at 20—30°C. Taken with the high speed of the photosensitive layer requiring exposure times in the order of seconds, the present invention provides a rapid, highly reliable and convenient method for the formation of metal images.

A useful processing apparatus is, e.g., a common 4-tray processing station as used in the known four-bath silver halide stabilisation processing (see e.g. GB-P 1,243,180 filed October 11, 1967 by Gevaert-Agfa N.V.) more particularly the RAPIDOPRINT unit DD 1437 (RAPIDOPRINT is a trade-mark of AGFA-GEVAERT N.V. Belgium).

The present invention makes it possible to produce metal images with very high contrast and excellent resolution at low cost. So, mass production of microform images is made possible in simple manner at high speed and half-tone images with high screen dot quality can be produced in a simple inexpensive equipment at low unit cost.

The synthesis of the alkali-soluble polymeric binding agents is exemplified in the following preparations:

Preparation 1

The following solution was formed:

methyl methacrylate	40 g
methacrylic acid	10 g
4,4'-azo-bis-4-cyanovaleric acid	1.5 g
methanol	500 ml

This solution was refluxed for 24 hours under a nitrogen atmosphere while continuously stirring. After cooling the solution was poured into water. The white, powdery precipitate was isolated and was dried under vacuum. Yield: 45 g of co(methyl methacrylate/methacrylic acid), having an intrinsic viscosity in tetrahydrofuran (20°C) of 0.155 dl/g. The copolymer comprised 18.4% by weight of methacrylic acid units.

Preparation 2

A solution of 45g of methyl methacrylate, 5 g of methacrylic acid and 1.5 g of 4,4'-azo-bis-4-cyanovaleric acid in 500 ml of methanol was refluxed for 24 hours while stirring under a nitrogen atmosphere. After cooling the solution was poured into water and the white, powdery precipitate was isolated and dried under vacuum. Yield: 44 g of co(methyl methacrylate/methacrylic acid) having an intrinsic viscosity (20°C) in tetrahydrofuran of 0.124 dl/g and comprising about 10% by weight of methacrylic acid units.

Preparation 3

A solution of 800 g of methyl methacrylate, 200 g of methacrylic acid and 30 g of 4,4'-azo-bis-4-cyanovaleric acid in 10 l of acetone was refluxed for 24 hours while stirring under nitrogen atmosphere. After cooling a solution was obtained having a viscosity of 1.25 mPa.s at 20°C and having a copolymer concentration of 8%. This solution can be used as such, without it being necessary to separate the copolymer. The separated copolymer had an intrinsic viscosity in tetrahydrofuran (20°C) of 0.173 dl/g and comprised 18.3% by weight of methacrylic acid units.

The invention will be illustrated by some specific examples, which are essentially non-limiting for the invention. All percentages are by weight, unless otherwise indicated.

Example 1

The following solution was made:

copolymer solution of Preparation 3	100 ml
pentaerythritol triacrylate	4 g
2,6-di-t-butyl-p-cresol	0.012 g
methanol	40 ml
acetone	66 ml
ethylene glycol monomethyl ether	10 ml

To 11 ml portions of the above solution were added quantities of photopolymerisation initiator as indicated in the following table. The different coating compositions formed were applied to a layer of bismuth of 150 nm having an optical density of more than 4. This layer had been vapour deposited under vacuum onto a polyethylene terephthalate film of 0.1 mm.

The different coating compositions were coated 50 μm thick on the bismuth layer so that, after drying for 15 minutes at 80°C light-sensitive layers of 3 μm were formed.

The minimum time of exposure needed for reproduction was then determined. Exposure of the light-sensitive layers through an original line image occurred in a SPEKTRAPROOF apparatus of Siegfried Theimer GmbH with a doped 2000 W high pressure mercury vapour lamp. Processing occurred in a RAPIDOPRINT DD 1347 four bath unit in a total processing time of 30 seconds at 20—30°C.

The composition of the four baths was as follows:

1. contained 1 l of a 0.5% sodium hydroxide solution. The non-exposed portions of the light-sensitive layer were dissolved away,
2. contained 1 l of water for rinsing,
3. contained a solution of 90 g of $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 1 l of 2.5 N sulfuric acid. The bared portions of the bismuth layer were eliminated;
4. contained 1 l of water for rinsing.

In the first bath a 10% aqueous solution of potassium carbonate could be used as an alternative. Contrasting black and white images were obtained. The exposure times are summarized in the following table.

photopolymerisation initiator	quantity	minimum exposure time needed
Michler's ketone	0.06 g	20 s
Oxime ester of formula 1 above	0.06 g	20 s
Oxime ester of formula 2 above	0.06 g	25 s
Oxime ester of formula 3 above	0.06 g	30 s
Michler's ketone + oxime ester 1	0.015 g 0.045 g	4 s
Michler's ketone + oxime ester 2	0.015 g 0.045 g	7 s
Michler's ketone + oxime ester 3	0.015 g 0.045 g	15 s

It appears from the above that when adding Michler's ketone to an oxime ester, a synergistic effect on the photopolymerisation and insolubilisation was noticed. The exposure time of 20 to 30 seconds needed was reduced to 4 seconds in the most favourable combination.

Example 2

The photosensitive coating composition was composed as follows:

	copolymer of preparation 1	3.6 g	
	pentaerythritol triacrylate	1.8 g	
25	Michler's ketone	0.14 g	
	oxime ester of formula 1	0.40 g	
	2,6-di-t-butyl-p-cresol	0.0054 g	
	methanol	20 ml	
	methyl ethyl ketone	75 ml	30
30	ethylene glycol mono methyl ether	5 ml	

This coating composition was applied 50 μm thick to a bismuth layer as described in example 1 so that after drying for 15 minutes at 80°C a photosensitive layer of 3 μm was formed.

This layer was exposed for 5 seconds in the SPEKTRAPROOF apparatus through a negative original and developed as explained in example 1. A positive image was obtained.

After having been stored for 72 hours at 57°C and a relative humidity of 34% the photosensitive recording material retained its original ability of being processed and had the same sensitivity.

Example 3

To 10 ml of the coating composition of example 2, 5 ml of acetone were added. A layer was

applied on a bismuth layer as described in example 1 in such a way that after drying at 80°C for 15 minutes it was 2 μm thick. The photosensitive coating was exposed for 3 seconds as described in Example 1. The exposed material was processed as in example 1 with the difference that the first developing bath contained 1 l of 0.25% aqueous sodium hydroxide solution.

5 A positive image was formed. 5

Example 4

The coating composition for the photosensitive layer was composed as follows:

	copolymer of Preparation 1	1.5 g	
	pentaerythritol triacrylate	0.5 g	
10	Michler's ketone	0.05 g	10
	oxime-ester of formula 1	0.15 g	
	2,6-di-t-butyl-p-cresol	0.002 g	
	methanol	10 ml	
	methyl ethyl ketone	25 ml	
15	ethylene glycol monomethyl ether	1.6 ml	15

The composition was applied on a bismuth layer as described in example 1 to form a photosensitive layer of 3 μm when dry. The layer was exposed for 5 seconds as described in Example 1. The exposed material was processed as in example 1, with the difference that the first tray contained 1 l of 1.5% aqueous sodium hydroxide solution.

20 A positive image was obtained. 20

Example 5

The coating composition for the photosensitive layer was composed as follows:

	copolymer of preparation 2	3 g	
	pentaerythritol triacrylate	3 g	
25	2,6-di-t-butyl-p-cresol	0.006 g	25
	Michler's ketone	0.15 g	
	oxime ester of formula 1	0.45 g	
	methanol	30 ml	
	methyl ethyl ketone	75 ml	
30	ethyleneglycol monomethyl ether	5 ml	30

The composition was applied on a bismuth layer as described in example 1 to form a photosensitive layer of 3 μm when dry. The photosensitive layer was exposed for 2 seconds through a negative in the SPEKTRAPROOF apparatus described above. After dipping for 20 seconds in a 2% aqueous sodium hydroxide solution and rinsing with water, the material was conducted through the third and fourth bath of the DD 1437 apparatus of Example 1, wherein the bared bismuth parts were dissolved away, thereby forming a positive image of the original.

35 35

Example 6

The following coating composition was formed:

	copolymer of Preparation 1	2 g	
40	copolymer of Preparation 2	2 g	40
	pentaerythritol triacrylate	2 g	
	2,6-di-t-butyl-p-cresol	0.006 g	
	Michler's ketone	0.15 g	
	oxime ester of formula 1	0.45 g	
45	methanol	30 ml	45
	methyl ethyl ketone	75 ml	
	ethylene glycol monomethyl ether	5 ml	

Upon formation of a 3 μm thick dry layer on the bismuth layer, exposure for 2 seconds through a negative as in Example 1, and processing as in Example 1, the first bath of the processing apparatus being formed by 1 l of 1.5% aqueous sodium hydroxide solution, a positive image was formed.

50 50

Example 7

The exposed film of Example 6 was only conducted through the first and second bath of the DD 1437 apparatus, used in example 6, so that only the non-exposed parts of the photosensitive layer had been washed away.

55 The processed film was rubbed in with a 2% aqueous phosphoric acid solution, whereby the bared bismuth parts were made hydrophilic. The film could now be used as a printing plate in offset-printing, the hardened parts of the resist taking up ink. 5000 prints could be made easily. 55

Example 8

The coating composition described in example 6 was applied on an aluminium plate to form thereon after drying a 3 μ m thick layer. This layer was exposed for 2 seconds through a negative as described in Example 1 and processed in the first and second bath of the DD 1437 apparatus as used in example 7. Only the non-exposed parts of the photosensitive layer were washed away. Just as in example 7 the processed aluminium plate was then rubbed in with a 2% aqueous phosphoric acid solution so that the bared aluminium parts were made hydrophilic. The plate could now be used as a printing plate in offset-printing.

Examples 9 to 16

The coating composition for the photosensitive layer was composed as follows:

	alkali-soluble copolymer	see table	
	plurally unsaturated monomer	see table	
	Michler's ketone	0.075 g	
	oxime-ester-of-formula 1	0.225 g	
15	2,6-di-t-butyl-p-cresol	0.003 g	15
	methanol	10 ml	
	methyl ethyl ketone	40 ml	
	ethylene glycol monomethyl ether	5 ml	

The coating compositions were coated on the bismuth layer applied to a polyethylene terephthalate film as described in example 1, so that after drying at 80°C for 15 minutes a photosensitive layer of 3 μ m thick was formed.

The photographic recording material was exposed through a negative in the SPEKTRAPROOF apparatus described above and processed in the DD 1437 apparatus of example 1.

In examples 9, 10 and 11 the first developing bath contained a 1% aqueous sodium hydroxide solution. In examples 11, 12, 13 and 15 a 0.5% solution was used and in example 14 a 2% solution was used. The other baths were composed as described in example 1.

The alkali-soluble copolymer, the plurally unsaturated monomer in the different examples and the minimum time of exposure needed to form a good positive image are given in the following table.

Example	alkali-soluble copolymer	amount	plurally unsaturated monomer	amount	minimum exposure needed
9	copolymer of preparation 1	2 g	triethylene glycol diacrylate	1 g	10 s
10	id.	2.25 g	id.	0.75 g	10 s
11	id.	2 g	triethylene glycol dimethacrylate	1 g	15 s
12	id.	2.25 g	id.	0.75 g	10 s
13	id.	2 g	trimethylolpropane trimethacrylate	1 g	3 s
14	id.	2.25 g	id.	0.75 g	5 s
15	id.	2 g	pentaerythritol tetraacrylate	1 g	4 s
16	id.	2.25 g	id.	0.75 g	4 s

30 Examples 17 to 19

Copolymers of methyl methacrylate and methacrylic acid (84:16 % by weight) but having different molecular weights were tested as follows:

coating compositions were formed containing:

	binding copolymer	2 g	
35	pentaerythritol triacrylate	1 g	35
	Michler's ketone	0.075 g	

oxime ester of formula 1	0.225 g
2,6-di-t-butyl-p-cresol	0.003 g
acetone	70 ml
ethylene glycol monomethyl ether	12 ml

5 In Example 17 the copolymer used had an intrinsic viscosity in tetrahydrofuran (at 20°C) of 0.165 dl/g. In Example 18, the intrinsic viscosity was 0.23 dl/g (at 20°C) and in Example 19 it was 0.40 dl/g (at 20°C).

The coating compositions were applied on a polyethylene terephthalate film that had been previously provided with a bismuth layer as described in example 1. Coating was such that after drying a photosensitive layer of 2 μ m resulted.

The three different recording materials were exposed for 5 seconds in a SPEKTRAPROOF apparatus as described above, exposure occurring through a step-wedge with a 0.15 constant. For processing a DD1437 apparatus was used the first bath containing a 0.5 % sodium hydroxide solution, the other baths being composed as indicated in Example 1.

15 The sensitivity of the recording materials is indicated in the following table.

Example	Intrinsic viscosity dl/g	Number of steps reproduced
17	0.165	5
18	0.23	7
19	0.40	8

It could be concluded from the above table that the sensitivity of the recording material increased with increasing intrinsic viscosity, thus with increasing molecular weight of the alkali-soluble binding copolymer. However, in Examples 18 and 19 the exposed parts were not completely dissolved away, although they became permeable for the etching liquid. The reason therefore was that in these Examples 18 and 19 the molecular weight of the copolymer was already too high, so that it became impossible to dissolve away the non-exposed parts in the 7 seconds allowed for developing in the apparatus.

As indicated in the description the intrinsic viscosity of the copolymer is preferably comprised between 0.05 and 0.20 dl/g.

Example 20

The following solution was prepared:

10% aqueous solution of co(methyl methacrylate-methacrylic acid) (82.5:17.5 by weight) having an intrinsic viscosity of 0.19 dl/g	20 ml
10% solution in acetone of pentaerythritol triacrylate	10 ml
0.1% solution in acetone of 2,6-di-t-butyl cresol	3 ml
1% solution in acetone of oxime ester of formula 1	15 ml
acetone	45 ml
ethyleneglycol monomethyl ether	15 ml

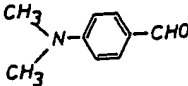
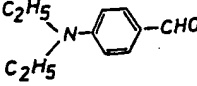
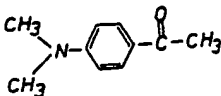
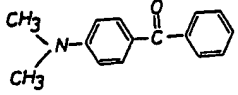
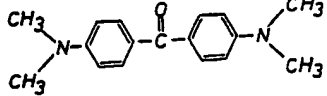
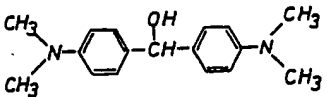
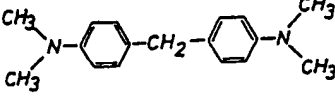
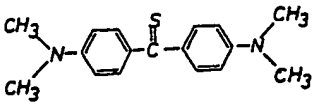
40 5 mg of a dialkylamino benzene as indicated in the following table were added to 11 ml amounts of the above solution and the solutions formed were coated on a bismuth layer which had been vapour deposited on a polyethylene terephthalate film. Coating was such that after drying for 15 minutes at 80°C a photosensitive layer of about 1.5 μ m was obtained.

The different photosensitive layers were exposed for 20 seconds in a SPEKTRAPROOF apparatus as described above using an iron (III) chloride doped high pressure mercury vapour lamp of 2000 Watt. Exposure occurred through a step-wedge with a 0.15 constant.

A DD 1437 apparatus was used for processing, the first bath of which contained 1 liter of a 1% sodium hydroxide solution. The three other baths were composed as in Example 1.

In the following table the number of reproduced steps are given. It is to be noted that in test No. 1 the photosensitive layer contained only as initiator the oxime ester of formula 1, and no dialkylamino

benzene was added. In tests Nos. 2 to 4, dialkylamino benzenes were added that do not correspond to the formula given above.

Test no.	dialkylamino benzene	number of steps reproduced
1	none	1
2		1
3		1
4		1
5		10
6		12
7		10
8		4
9		7

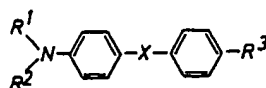
It could be concluded that the addition of a dialkylamino benzene that does not correspond to the formula of the dialkylamino benzenes given above, had no influence at all on the photopolymerisation. The number of steps reproduced was the same in tests 2 to 4 as in test no. 1, wherein the dialkylamino benzene was absent.

On the contrary dialkylamino benzenes which correspond to the given formula, had a synergistic effect on the photopolymerisation, as showed by the number of reproduced steps indicated for tests 5 to 9 in the table. The best results, namely 12 steps were found in test no. 6 when using Michler's ketone as dialkylamino benzene.

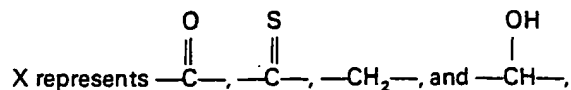
When replacing the ketoxime ester of formula 1 by that of formula (4) and using as dialkylamino benzene Michler's ketone the number of reproduced steps is 10.

CLAIMS

1. A photosensitive material which comprises a base having thereon a photosensitive layer comprising a polymerisable ethylenically unsaturated organic compound or compounds and an oxime ester photopolymerisation initiator characterised in that the layer contains as additional polymerisation initiator a p-dialkylamino benzene corresponding to the formula:



wherein:

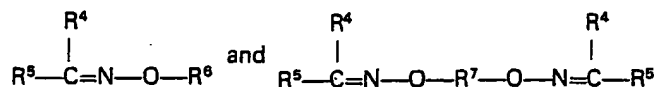


each of R^1 and R^2 , the same or different, represents a lower alkyl group, and

5 R^3 represents a hydrogen atom, an alkyl group, an alkoxy group or a $N(R^1)(R^2)$ group wherein each of R^1 and R^2 has one of the above meanings. 5

2. A photosensitive material according to claim 1, wherein the dialkylamino benzene is Michler's ketone.

3. A photosensitive material according to claim 1 or 2, wherein the oxime ester
10 photopolymerisation initiator corresponds to one of the formulae: 10



wherein:

R^4 represents an alkyl group of 1 or 2 carbon atoms, an aryl group, an alkaryl group, an aralkyl group, a hydroxy-substituted aralkyl group, or an unsubstituted or substituted acyl group,

15 R^5 represents a hydrogen atom, an alkyl group of 1 or 2 carbon atoms, an aryl group or an unsubstituted or substituted acyl group, or wherein 15

R^4 and R^5 together represent the atoms necessary to form with the adjacent carbon atom a cycloalkyl group, a phenanthrone group, or an indanone group,

R^6 represents an unsubstituted or substituted acyl group, and

20 R^7 represents a diacyl group. 20

4. A photosensitive material according to claim 3, wherein at least one of R^4 and R^5 is unsubstituted or substituted acyl.

5. A photosensitive material according to any of claims 1 to 4, wherein the oxime ester compound is one of the compounds identified herein.

25 6. A photosensitive material according to any of claims 1 to 5, wherein the polymerisable ethylenically unsaturated organic compound is a plurally unsaturated polymerisable compound. 25

7. A photosensitive material according to claim 6, wherein the plurally unsaturated polymerisable compound is pentaerythritol triacrylate.

8. A photosensitive material according to any of claims 1 to 7, wherein the photosensitive layer
30 also comprises a polymeric binding agent. 30

9. A photosensitive material according to claim 8, wherein the polymeric binding agent is an alkali-soluble polymer.

10. A photosensitive material according to claim 9, wherein the alkali-soluble polymer is a copoly(methyl methacrylate-methacrylic acid) wherein the ratio by weight between the methyl
35 methacrylate and the methacrylic acid units varies between about 90:10 and about 75:25 and said copolymer has an intrinsic viscosity measured in tetrahydrofuran at 20°C comprised between about 0.05 and about 0.20 dl/g. 35

11. A photosensitive material according to claim 9 or 10, wherein in the photosensitive layer the ratio by weight between the alkali-soluble binding agent and the ethylenically unsaturated polymerisable compound is comprised between 1:2 and 5:1. 40

12. A photosensitive material according to any of the preceding claims 9 to 11, wherein in the photosensitive layer the oxime ester compound is present in an amount of 5—7.5% by weight, and the dialkylamino benzene is present in an amount of 1.5—2.5% by weight, reckoned on the joint weight of unsaturated polymerisable compound and of alkali-soluble binding agent.

45 13. A photosensitive material according to any of the preceding claims, wherein the base is a highly opaque metal coating on a film support. 45

14. A photosensitive material according to claim 13, wherein the base is composed of a polyethylene terephthalate film support provided with a bismuth coating.

15. A photosensitive material according to claim 1 and substantially as described herein.

50 16. A photosensitive material according to claim 1 and substantially as described in any of the examples herein. 50

17. A recording method comprising the steps of:
- (1) information-wise exposing the photosensitive layer of the photosensitive material of any of claims 1 to 16 to actinic radiation, whereby in the exposed areas the ethylenically unsaturated compound or compounds is or are polymerised (copolymerised) and
 - 5 (2) selectively removing the non-exposed or insufficiently exposed portions of the photosensitive layer by means of a solvent for the said unsaturated compound(s).
18. A method according to claim 17, wherein the photosensitive layer is information-wise exposed to actinic light of wavelengths ranging from 250 to 400 nm.
- 10 19. A recording method according to claim 17 or 18, wherein the photosensitive material is a photosensitive material according to claim 13 or 14, and wherein the exposed material is first overall contacted with an aqueous alkaline liquid to remove selectively the non-exposed or insufficiently exposed portions of the photosensitive layer, and then the bared portions of the opaque metal layer are contacted with a liquid that is capable of chemically removing said portions without removing the exposed portions of the photosensitive layer.
- 15 20. A method according to claim 19, wherein the aqueous alkaline liquid is a 0.4 to 7.5% by weight aqueous solution of potassium hydroxide, or a 0.25 to 5% by weight aqueous solution of sodium hydroxide.
21. A method according to claim 19 or 20, wherein the opaque metal layer is a bismuth layer and the bared portions are removed with a 5—20% aqueous solution of iron (III)-chloride.
- 20 22. A method according to claim 21, wherein the aqueous solution of iron (III)-chloride contains 0.25—1% by weight of citric acid.
23. A method according to claim 19 or 20, wherein the opaque metal layer is a bismuth layer and the bared portions are removed with an aqueous solution containing 3 to 6% by weight of hydrogen peroxide and 5 to 10% by weight of sulphuric acid.
- 25 24. A method according to claim 17 and substantially as described herein.
25. A method according to claim 17 and substantially as described in the examples herein.